

**We Claim:**

1. A bi-functional catalyst useful for oxidation and removal of nitrogen oxides ( $\text{NO}_x$ ) contained in fuel combustion gases, the catalyst comprising:

an adsorption function metal oxide component selected from the group consisting of the metals barium, cesium, lanthanum, strontium and zirconium, and combinations thereof for providing adsorption function and sites for the nitrogen oxides in the combustion gases; and

an oxidation function metal oxide component selected from the transition metals group consisting of chromium, cobalt, copper, iron, manganese and platinum and combinations thereof for providing an oxidation function and sites closely adjacent to said adsorption metal oxide component and sites for the nitrogen oxides in the combustion gases, said adsorption metal oxide and said oxidation metal oxide being combined together in close intimate contact so that said adsorption metal oxide component and said oxidation metal oxide component are chemically bonded closely together so as to form a metal oxide complex having a crystalline structure, with the molar ratio of the adsorption metals to the oxidation metals being in a ratio range of 0.1:1 to 5:1 to provide the bi-functional catalyst.

2. The bi-functional catalyst of claim 1, wherein said oxidation function metal oxide component includes copper, manganese, and platinum, and the molar ratio of said adsorption metals to the oxidation metals is in a range of about 0.2:1 to 2:1.
3. The bi-functional catalyst of claim 1, wherein said adsorption function metal oxide component is barium (Ba) or lanthanum (La), and said metal oxide oxidation component is copper (Cu) and manganese (Mn) promoted with platinum (Pt).
4. The bi-functional catalyst of claim 2, wherein said adsorption metal oxide component is lanthanum (La), and said oxidation metal oxide components are copper (Cu) and manganese (Mn) promoted with platinum (Pt).

5. The bi-functional catalyst of claim 2, wherein said adsorption metal oxide component is barium (Ba), and said oxidation metal oxide component is copper (Cu) and manganese (Mn) promoted with platinum (Pt).
6. The bi-functional catalyst of claim 1, wherein said adsorption and oxidation metal oxides in powder form are provided on a porous support material having surface area of at least about 50 m<sup>2</sup>/g.
7. A bi-functional catalyst useful for oxidation and removal of nitrogen oxides (NO<sub>x</sub>) contained in fuel combustion gases, the catalyst comprising:

an adsorption function metal oxide component of barium or lanthanum selected for providing adsorption function and sites for the nitrogen oxides in the combustion gases; and

an oxidation function metal oxide component selected from the group consisting of copper, manganese and platinum for providing oxidation function and sites closely adjacent to said adsorption metal oxide component and sites for the nitrogen oxides in the combustion gases, said adsorption metal oxides and said oxidation metal oxides being combined intimately together so that said adsorption metal oxide component and said oxidation metal oxide component are chemically bonded closely together so as to form a metal oxide complex having a crystalline structure, with the molar ratio of the adsorption metals to the oxidation metals being in a range of 0.2:1 to 2:1, said metal oxides being provided on a porous inert support material having surface area of 50-500 m<sup>2</sup>/g to provide the bi-functional catalyst.

8. A method for making a bi-functional catalyst suitable for catalytic oxidation of nitrogen oxides (NO<sub>x</sub>) contained in fuel combustion gases, comprising the steps of:
  - (a) providing an aqueous solution of adsorption function metal ions selected from the metals group consisting of barium, cesium, lanthanum, strontium and zirconium and combinations thereof for providing an adsorption function and sites for adsorbing nitrogen oxide contained in combustion gases;

- (b) providing an aqueous solution of oxidation function metal ions selected from the metals group consisting of chromium, cobalt, copper, iron, manganese and platinum for providing an oxidation function and sites for oxidizing nitrogen oxides in combustion gases, said adsorption function metals having a molar ratio to the oxidation function metals in the range of 0.1:1 to 5:1;
- (c) mixing said adsorption and oxidation function metal ion solutions together and adding a binding agent acid having at least two functional groups selected for providing close intimate contact of said metal ions and thereby providing a precursor solution;
- (d) drying said metal ions precursor solution and heating to a temperature of 500-800°C (930-1470°F) for 0.4-5 hours and thereby forming a metal oxide complex precursor material, then cooling the metal oxide complex precursor material; and
- (e) forming a second solution of oxidation function metal ions and a platinum salt, and impregnating said precursor material with said second solution, into, then drying and calcining the impregnated precursor material at 500-800°C temperature and cooling to provide the bi-functional catalyst.

9. The method for making a bi-functional catalyst of claim 8, wherein the binding agent acid is carboxylic acid having a molar ratio of acid to total metals in a range of 0.5:1 to 2:1.
10. The method for making a bi-functional catalyst of claim 9, wherein the carboxylic binding acid is citric acid.
11. The method for making a bi-functional catalyst of claim 9, wherein the carboxylic binding agent is sodium citrate.
12. A method for making a bi-functional catalyst suitable for catalytic oxidation of nitrogen oxides (NO<sub>x</sub>) contained in fuel combustion gases, comprising the steps of :
  - (a) providing an aqueous solution of adsorption function metal ions selected from the metals group consisting of barium (Ba) and lanthanum (La) for providing an adsorption function and sites for adsorbing nitrogen oxides contained in combustion gases;

- (b) providing an aqueous solution of oxidation function metal ions selected from the metals group consisting of copper (Cu) and manganese (Mn) for providing an oxidation function and sites for oxidizing nitrogen oxides contained in combustion gases, said adsorption metals having a molar ratio to the oxidation function metals in the range of 0.1:1 to 5:1;
- (c) mixing said adsorption and oxidation function metal ion solutions together and adding a binding agent acid having at least two functional groups for providing close intimate contact of said metal ions and thereby providing a precursor solution;
- (d) drying said metal ions precursor solution and heating to a temperature of 500-800°C (930-1470°F) for 0.4-5 hours and thereby forming a metal oxide complex precursor material, then cooling the metal oxide complex precursor material; and
- (e) forming a second solution of manganese (Mn) ions and a platinum (Pt) salt, and impregnating said metal oxide complex precursor material with the second solution, then drying and calcining the impregnated precursor material at 500-800°C temperature and cooling to provide the bi-functional catalyst.
13. The method for making a bi-functional catalyst of claim 12, wherein said adsorption function metal is barium (Ba).
14. The method for making a bi-functional catalyst of claim 12, wherein said adsorption function metal is lanthanum (La).
15. The method for making a bi-functional catalyst of claim 12, wherein said adsorption function metal is barium (Ba) and said oxidative function metal is copper (Cu) and manganese (Mn) promoted with platinum (Pt).
16. The method for making a bi-functional catalyst of claim 8, including depositing the catalyst in powder form onto a porous support material.
17. A process for catalytic oxidation and removal of nitrogen oxides (NO<sub>x</sub>) contained in fuel combustion gases, the process comprising:

- (a) providing a combustion gas stream containing nitrogen oxides ( $\text{NO}_x$ ) not exceeding about 0.5 vol% together with 5-10 vol.% oxygen; and
  - (b) contacting said combustion gas stream with a bi-functional oxidation catalyst as defined by claim 1, said catalyst being capable of adsorbing and oxidizing the nitrogen oxides ( $\text{NO}_x$ ) in said combustion gas stream at 170-550° F temperature and 0.5-20 psig pressure and space velocity of 5,000-100,000  $\text{hr}^{-1}$  to form higher oxides of nitrogen and providing a treated combustion gas stream containing partially oxidized  $\text{NO}_x$ .
18. The catalytic oxidation process of claim 17, wherein said combustion gas stream contains up to 0.2 vol. %  $\text{NO}_x$ .
19. The catalytic oxidation process of claim 17, wherein the catalytic oxidation conditions are 220-350° F temperature, 1-15 psig pressure, and space velocity of 8,000-50,000  $\text{h}^{-1}$  and the  $\text{NO}_x$  concentration in the treated combustion gas stream is at least about 50 vol %  $\text{NO}_2$ .
20. The catalytic oxidation process of claim 19, wherein the  $\text{NO}_x$  in the treated combustion gas stream contains 60-98 vol %  $\text{NO}_2$ .
21. A process for catalytic oxidation and removal of nitrogen oxides ( $\text{NO}_x$ ) from hydrocarbon fuel combustion exhaust gases, the process comprising:
- (a) providing a combustion gas stream containing nitrogen oxides ( $\text{NO}_x$ ) not exceeding about 0.5 vol % together with 5-10 vol % oxygen;
  - (b) contacting said combustion gas stream with an oxidation catalyst as defined by claim 1 and which is capable of adsorbing and oxidizing the  $\text{NO}_x$  to form higher oxides of nitrogen at reaction conditions of 170-550°F temperature, 0.5-20 psig. pressure, and space velocity of 5,000-100,000  $\text{hr}^{-1}$ , and providing an initially treated gas stream containing partially oxidized  $\text{NO}_x$ ;
  - (c) contacting said treated gas stream containing partially oxidized  $\text{NO}_x$  with a chemical oxidant sufficient to provide a molar ratio of said chemical oxidant to  $\text{NO}_x$  in a range of 0.5:1 to 1.2:1 and further oxidizing the  $\text{NO}_x$  to higher oxides of nitrogen;
  - (d) scrubbing the treated combustion gas containing  $\text{NO}_2$  and higher oxides of nitrogen

by contacting the combustion gas with a scrubbing liquid, and removing the higher oxides of nitrogen from the gas by absorbing the nitrogen oxides in the scrubbing liquid;

- (e) removing from said liquid scrubbing step a further treated combustion gas stream containing less than about 15 ppm  $\text{NO}_x$  and discharging the further treated gas stream to the atmosphere; and
  - (f) withdrawing from said liquid scrubbing step a major portion of the scrubbing liquid containing absorbed nitrogen oxides.
22. The catalytic oxidation process claim 21, wherein said combustion gas stream contains up to 0.2 vol. %  $\text{NO}_x$ .
23. The catalytic oxidation process of claim 21, wherein the catalytic oxidation conditions are 200-500°F temperature, 1.0-15 psig pressure, and space velocity of 8,000-50,000  $\text{h}^{-1}$ , and the  $\text{NO}_x$  in the initially treated gas stream is at least about 50 vol %  $\text{NO}_2$ .
24. The catalytic oxidation process of claim 21, wherein the chemical oxidation reaction conditions are 100-250°F temperature and 0.8-1.4 psig pressure.
25. The catalytic oxidation process of claim 21, wherein said chemical oxidant is ozone ( $\text{O}_3$ ) and the molar ratio of ozone ( $\text{O}_3$ ) to the combustion gas  $\text{NO}_x$  is 0.8:1 to 1.0:1.
26. The catalytic oxidation process of claim 21, wherein said scrubbing liquid is water.
27. The catalytic oxidation process of claim 21, wherein said oxidation catalyst is a bi-functional oxidation catalyst as defined by claim 1 and the catalytic oxidation temperature is 300-350°F.
28. The catalytic oxidation process of claim 27, wherein the final treated combustion gas removed at step (e) contains less than about 10 ppm  $\text{NO}_x$ .

29. A process for catalytic oxidation and removal of nitrous oxides ( $\text{NO}_x$ ) from hydrocarbon fuel combustion exhaust gases, the process comprising:
- (a) providing a combustion gas stream containing 0.05-0.2 vol % nitrogen oxides ( $\text{NO}_x$ ) together with 5-10 vol % oxygen.
  - (b) contacting said combustion gas stream with a bi-functional oxidation catalyst as defined in claim 1, said catalyst being capable of adsorbing and oxidizing the  $\text{NO}_x$  contained in said combustion gas stream to form at least about 50 vol %  $\text{NO}_2$ , at 300-500°F temperatures, 1-15 psig. pressure, and space velocity of 8,000-50,000  $\text{hr}^{-1}$ ; and providing an initially treated combustion gas;
  - (c) contacting said initially treated combustion gas stream containing partially oxidized  $\text{NO}_x$  with sufficient ozone ( $\text{O}_3$ ) oxidant to provide a molar ratio of the  $\text{O}_3$  to  $\text{NO}_x$  of 0.5:1 –1.0:1, and at 100-250°F temperature and further oxidizing the  $\text{NO}_2$  to provide a further treated combustion gas containing essentially  $\text{N}_2 \text{O}_5$ ;
  - (d) scrubbing the further treated combustion gas containing essentially  $\text{N}_2 \text{O}_5$  by contacting the gas with water and removing the higher oxides of nitrogen from the combustion gas by absorbing the nitrogen oxides in the water;
  - (e) removing from said liquid scrubbing step the further treated combustion gas stream containing less than about 10 ppm  $\text{NO}_x$ , and discharging said further treated combustion gas stream to the atmosphere; and
  - (f) withdrawing from said liquid scrubbing step a major portion of the scrubbing liquid containing absorbed nitrogen oxides.